

In Situ Geochronology on Mars and the Development of Future Instrumentation

Barbara A. Cohen,¹ Charles A. Malespin,¹ Kenneth A. Farley,² Peter E. Martin,²
Yuichiro Cho,¹ and Paul R. Mahaffy¹

Abstract

We review the *in situ* geochronology experiments conducted by the Mars Science Laboratory mission's Curiosity rover to understand when the Gale Crater rocks formed, underwent alteration, and became exposed to cosmogenic radiation. These experiments determined that the detrital minerals in the sedimentary rocks of Gale are ~4 Ga, consistent with their origin in the basalts surrounding the crater. The sedimentary rocks underwent fluid-moderated alteration 2 Gyr later, which may mark the closure of aqueous activity at Gale Crater. Over the past several million years, wind-driven processes have dominated, denuding the surfaces by scarp retreat. The Curiosity measurements validate radiometric dating techniques on Mars and guide the way for future instrumentation to make more precise measurements that will further our understanding of the geological and astrobiological history of the planet. Key Words: Mars—Mars rovers—Geochronology—Instrument development. Astrobiology 19, 1303–1314.

1. Introduction

THE MARS SCIENCE Laboratory mission is exploring an astrobiologically relevant ancient environment on Mars to decipher its geological processes and history, including an assessment of past habitability. The search for life in the Solar System depends on discovering the right moments in planetary evolution—when habitable environments existed, when they declined, and when geological processes operated to preserve traces of life after death. However, the relative martian chronology derived from stratigraphy is not yet tied to an absolute chronology.

The existing understanding of martian chronology is based primarily on crater density and analogy with the Moon, under the assumptions that the lunar cratering history is well constrained and that the martian flux rates can be derived from the lunar rate. However, the relative cratering rate between the Moon and Mars is far from established; the lunar crater record itself conveys a roughly billion-year uncertainty during the Hesperian, and additionally the martian impact flux could have ranged from the same as the Moon to up to five times higher (Robbins, 2014; Bottke and Norman, 2017). Confounding variables that contribute to the uncertainties asso-

ciated with dating by crater density on Mars range from the contributions of persistent volcanism (McEwen *et al.*, 1999; Hartmann *et al.*, 1999; Keszthelyi *et al.*, 2008) and fluvial and aeolian weathering (Tanaka *et al.*, 2014a,b; Greeley *et al.*, 2001) to the preservation of impact craters on Mars.

Absolute ages of martian surface units are, therefore, uncertain—a factor of two or more on older surfaces (Hartmann and Neukum, 2001), and disagreements can be an order of magnitude or more on younger, lightly cratered surfaces (Swindle *et al.*, 2004). Our incomplete knowledge of absolute martian geochronology limits our ability to understand the timing or martian evolutionary milestones (Doran, 2004). For example, we do not know whether the crucial Noachian-Hesperian boundary, where a warm, wet Mars became arid (Bibring *et al.*, 2006), occurred before, after, or concurrent with the Late Heavy Bombardment on the Moon and the oldest intact rocks on Earth (*e.g.*, Bottke and Norman, 2017), so martian climate change cannot yet be put into the context of Solar System history.

Though not a baselined investigation, the Curiosity rover has demonstrated an ability to measure K-Ar and cosmic-ray exposure (CRE) ages for rocks within Gale Crater (Farley *et al.*, 2014; Vasconcelos *et al.*, 2016; Martin *et al.*, 2017).

¹Solar System Exploration Division, NASA Goddard Space Flight Center, Greenbelt, Maryland.

²Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, California.

In situ dating significantly enhances the ability of Curiosity to meet its science objectives by enabling targeted searches for ancient environments that are conducive to life in timeframes that may have been astrobiologically relevant.

In situ dating determines the age and exposure history of lithologic units to understand when they formed, underwent alteration, and/or became exposed on the martian surface, and to use these dates to place the geological environment of Gale Crater into the context of planet-wide geological, atmospheric, and climate history. The K-Ar age also provides the last time the rock was significantly heated, and exposure ages tell how long it has been within a meter of the surface, both of which are important constraints on biosignature preservation potential. The current, thin martian atmosphere provides little protection from solar ultraviolet radiation and cosmic-ray bombardment, degrading organic molecules in the near surface if exposed for more than a few millions of years (Myr) (Dartnell, 2011; Pavlov *et al.*, 2012; Eigenbrode *et al.*, 2018).

2. Setting and Experiments

Curiosity accomplishes *in situ* dating by using the potassium (K)-Argon (Ar) radiometric dating system, based on the decay of ^{40}K (0.0117% of all naturally occurring K) to ^{40}Ar . The amount of radiogenic ^{40}Ar that a rock contains is related to the amount of K that the rock contains and the length of time that the rock has been solid enough and cool enough to retain argon—for example, when it cooled and crystallized or was deposited from fluid. Many rocks and minerals on the martian surface lend themselves to K-Ar dating, as has been demonstrated by successful K-Ar application to martian meteorites and weathering products (Swindle *et al.*, 1995; McSween and Treiman, 1998; Nyquist *et al.*, 2001; Walton *et al.* 2007, 2008).

The rover technique measures the parent K in the solid state by using the Alpha Particle X-Ray Spectrometer (APXS) to determine its abundance by weight; then, noble gases are released by heating, and their abundance is measured with the Sample Analysis at Mars (SAM) quadrupole mass spectrometer (Farley *et al.*, 2014; Vasconcelos *et al.*, 2016; Martin *et al.*, 2017). The relative (parent) and absolute (daughter) measurements are related by measuring the mass of the sample. Though Curiosity has no method with which to directly measure the sample mass, a reasonable estimate can be developed by using relevant parameters from the rover's Collection and Handling for *In-Situ* Martian Rock Analysis (CHIMRA) device. The interpretation of the K-Ar age depends critically on the origin of the potassium-bearing phases. Therefore, the mineralogy of the sample from the Chemistry and Mineralogy (CheMin) instrument is used to apportion K among relevant mineral phases weighted by the potassium content of the minerals.

In addition to ^{40}Ar from decay, isotopes of helium, neon, and argon are produced in rocks at the surface of Mars by interaction between cosmic-rays and rock-forming elements. The surface exposure age is a measure of the time elapsed since a rock became exposed to cosmic-rays by denudation. Useful cosmogenic noble gas isotopes include ^3He , ^{21}Ne , ^{38}Ar , ^{83}Kr , and ^{126}Xe produced by galactic cosmic-rays and ^{80}Kr , ^{36}Ar , and ^{128}Xe from neutron capture at the martian surface (Eugster *et al.*, 1998; Rao *et al.*, 2002; Wieler, 2002).

Curiosity measures three cosmogenic nuclides: ^3He and ^{21}Ne that are produced via spallation of O, Mg, Si, and Al (held mostly in detrital grains), and ^{36}Ar that can be produced by spallation on Ca, K, and Fe in the detrital grains as well as from neutron capture of ^{35}Cl associated with secondary phases in sedimentary rock. Only neutron capture is included in the production rate models, as it generates orders of magnitude more ^{36}Ar than spallation processes.

Curiosity has performed K-Ar and cosmogenic noble gas experiments at three sites along the Gale Crater traverse so far (Fig. 1). Gale Crater formed in the late Noachian to early Hesperian (Anderson, 2010; Thomson *et al.*, 2011). The area surrounding Gale comprises a rich and diverse geological history, including volcanic activity (Stolper *et al.*, 2013; Schmidt *et al.*, 2014), impact modification (Newsom *et al.*, 2015), aqueous alteration (Ehlmann and Buz, 2015), and fluvial and lacustrine sedimentary environments (Williams *et al.*, 2013; Grotzinger *et al.*, 2014). Three experiments were accomplished by using the drill and CHIMRA to deliver a crushed and sieved sample of sedimentary rock to the SAM cups, and the ages and cosmogenic abundances have been published.

The first experiment was run at the Cumberland member of the Yellowknife Bay formation. A substantial expanse of bare bedrock was encountered in an ~5-m-deep topographic trough representing an erosional window through a sequence of stratified rocks known as the Yellowknife Bay formation. These rocks consist mostly of distal alluvial fan and lacustrine facies of basaltic bulk composition derived from the Gale Crater rim (Grotzinger *et al.*, 2014). The Sheepbed mudstone forms the floor of the bay and is overlain by the Gillespie Lake sandstone with a sharp contact that can be traced around the full width of the Yellowknife Bay trough. Curiosity sampled the top of the Sheepbed mudstone. The K-Ar age reflects the formation age of the components of the mudstone, whereas the cosmogenic age is a measurement of the exposure time of the mudstone as the Gillespie Lake member weathers away.

A second experiment was conducted at a target named Windjana in the Kimberley formation. The Kimberley formation sediments sit ~35 m topographically and stratigraphically above the Sheepbed mudstone. The Kimberley formed by deposition in a pro-grading, fluvio-deltaic system during the late Noachian to early Hesperian, before the existence of most of Mt. Sharp (Rice *et al.*, 2017). After deposition, the rocks underwent multiple episodes of diagenetic alteration with different aqueous chemistries and redox conditions, followed by significant aeolian abrasion. Elevated K_2O abundances were measured throughout the Kimberley formation, attributable to sanidine in the mineralogy, pointing to an alkali feldspar protolith. In Windjana, the K-Ar measurements primarily reflect the age of the sanidine, whereas the cosmogenic ages are the result of overburden removal of higher Mt. Sharp sediments.

The third experiment targeted the Mojave 2 mudstone in the Pahrump Hills region of the Murray Formation. As Curiosity began ascending the lower Mt. Sharp stratigraphic section, it encountered finely laminated mudstones and fine-grained sandstone interpreted to be distal lacustrine deposits that were deposited as the Gale Crater lake level rose (Grotzinger *et al.*, 2015). Curiosity drilled at Mojave 2, a finely laminated mudstone in the Pahrump Hills, with a

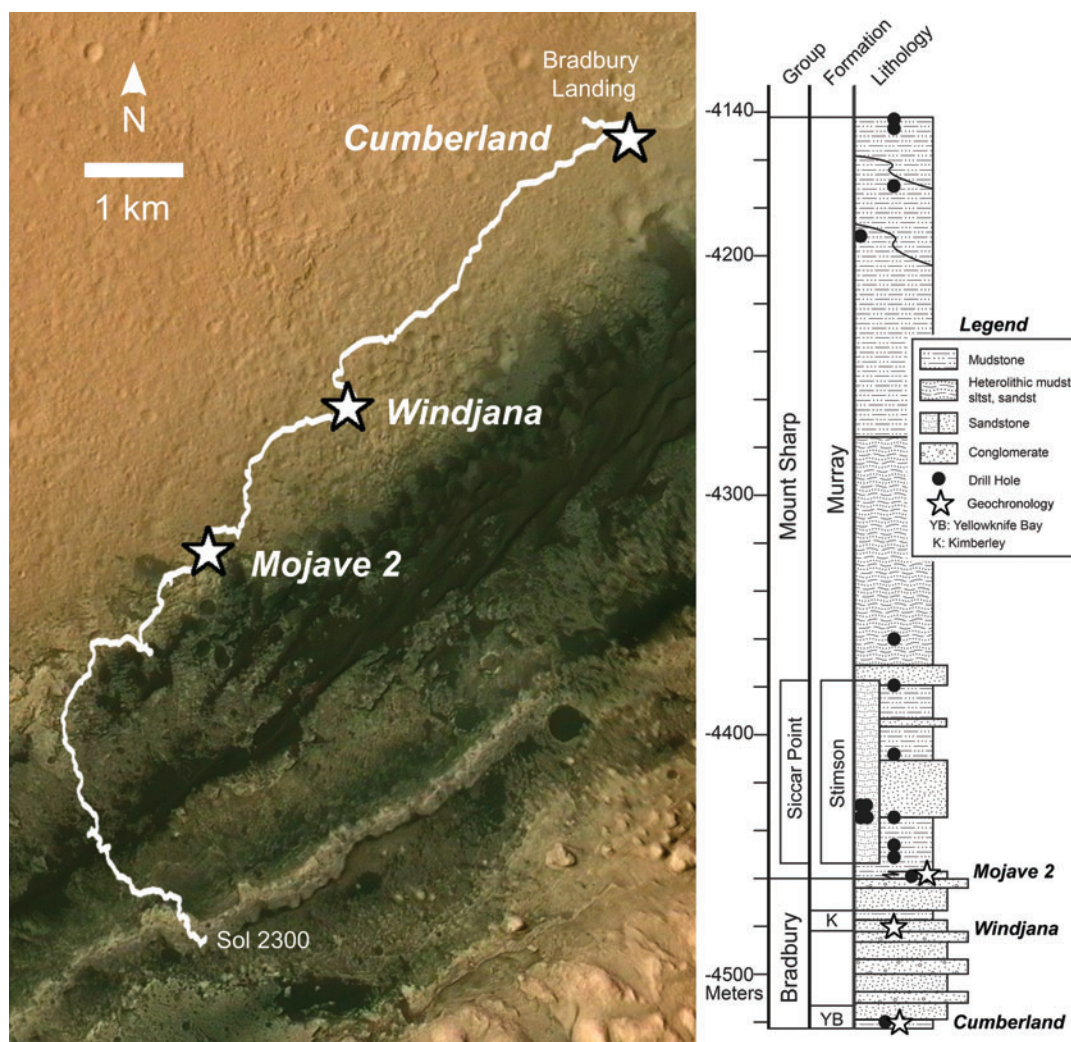


FIG. 1. Location of the three drilled samples used for Curiosity geochronology experiments, (1) along the rover traverse (base map: Mars Reconnaissance Orbiter Context Camera images colorized with Mars Express High Resolution Stereo Camera data, NASA/JPL/MSSS/ESA/DLR/FU Berlin [G. Neukum]/Tanya Harrison/Emily Lakdawalla) and (2) within the stratigraphic column (NASA/JPL-Caltech).

grain size too small to be resolved by the Mars Hand Lens Imager (MAHLI) ($<60\mu\text{m}$). This mudstone contains several weight percent jarosite $[\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6]$, making it the most jarosite-rich sample yet discovered by Curiosity (Rampe *et al.*, 2017). This target represented a good opportunity to separate the authigenic and detrital components of the mudstone with a two-step heating experiment, where the K-Ar age would date the authigenic jarosite at low temperatures and detrital feldspar at higher temperatures, whereas the cosmogenic age should reflect the removal of Mt. Sharp overburden, similar to Windjana.

3. Results

3.1. K-Ar dating

Dating of the Cumberland sample yielded a K-Ar age of 4.21 ± 0.35 Ga (Farley *et al.*, 2014). Based on the mineralogy derived from CheMin, the majority of potassium was likely derived from the detrital components, which are typical of volcanic rocks: plagioclase, pyroxene, and minor olivine,

sanidine, and ilmenite. Assuming the detrital mineral assemblage represents a cogenetic suite, the bulk release of Ar from this sample can be used to calculate a straightforward K-Ar age that represents the formation of the parent basalt, which was physically weathered but not significantly chemically altered after its deposition into the mudstone.

The Windjana sample contained sanidine as the major K-bearing phase, also interpreted to be a detrital component of the sandstone (Le Deit *et al.*, 2016; Treiman *et al.*, 2016). Sanidine is known to be highly resistive to noble gas diffusion, requiring temperatures in excess of 1400°C for complete Ar extraction (*e.g.*, McDougall and Harrison, 1999). Experiments on terrestrial sanidine grains only released 5–10 wt % of their radiogenic argon at a temperature of $\sim 900^\circ\text{C}$, even after extended (17 h) heating (Cassata and Renne, 2013). Power limitations on the SAM noble gas release experiment preclude such long extraction times.

The first Windjana sample (WJ1) was heated to $\sim 915^\circ\text{C}$ for 25 min; therefore, it was disheartening but not completely surprising to learn that this sample released an Ar signal with a magnitude of about 5% of the Cumberland sample,

corresponding to an apparent age of 627 ± 50 Ma. To test whether the low gas yield was due to incomplete degassing, a second heating experiment at a higher oven voltage was performed on the same sample (WJ1-RE). The second heating released no further Ar, but whether the increase in voltage actually achieved a significant increase in sample temperature is unknown. A second aliquot from the same original drill-hole (WJ2) was later analyzed following the same procedures carried out during the analyses of the WJ1-RE sample, heating to the higher voltage setting for 25 min. This second aliquot released slightly more Ar than WJ1, yielding an apparent age of 1710 ± 110 Ma, but this is still too young to be interpreted as the detrital mineral age of the sandstone.

The most likely explanation of the young apparent ages in these samples is that the oven temperature was too low and the heating time too short to ensure complete extraction from the highly retentive sanidine phase. An additional complication may be that the ingested sample separated into a coarser fraction rich in sanidine (WJ1) and a fine-grained fraction richer in authigenic illite/smectite and amorphous components (WJ2) during handling in CHIMRA. The two aliquots would respond differently to heating, exacerbating differences in gas extraction, and potentially producing the discrepancy in K-Ar ages obtained for WJ1 and WJ2.

The third radiometric dating experiment took advantage of the two-step heating methodology used on Windjana to measure separate ages of the detrital and authigenic components of the Mojave 2 sample (Martin *et al.*, 2017). The Mojave 2 mineralogy comprises substantial amounts of both plagioclase and jarosite, both of which host K, but which have different Ar release temperatures. Jarosite releases Ar at temperatures less than 500°C , whereas plagioclase retains the vast majority of its Ar to above 500°C (Cassata *et al.*, 2009; Kula and Baldwin, 2011). Accordingly, an SAM experiment was devised to heat the Mojave 2 sample twice and validated by using the SAM testbed before its execution on Mars. The first part of the experiment heated the sample monotonically to $\sim 500^\circ\text{C}$ over 1 h to release argon from jarosite, and it measured the evolved gases in both dynamic and semi-static modes. The following sol, an identical procedure was followed for the second heating step, which reached a peak temperature of around 930°C , releasing radiogenic argon from plagioclase.

A mass-balance model, bounded with data from martian meteorites, was constructed to apportion the total K_2O in the sample, measured by APXS, to the plagioclase and jarosite measured by CheMin. Based on this model, plagioclase contains around 15% of the total K_2O in Mojave 2, with the remainder being carried predominately in the jarosite. Knowing that, the K_2O and the released radiogenic argon enable calculation of an age for each component. The 4.07 ± 0.63 Ga age of the detrital component is consistent with, though less precise than, the detrital component age of Cumberland. The 2.12 ± 0.36 Ga K-Ar age of the authigenic component was interpreted as jarosite formation in a post-depositional fluid environment, corroborated by the prevalent diagenetic features in Mojave 2 and the surrounding bedrock. The largest sources of uncertainty in the interpretation of these ages were the sample transfer model and the potassium distribution model, discussed in more detail in the next section.

The Aeolis Palus sedimentary sequence hosting the dated samples has a crater-count age of approximately 3.4–3.2 Ga

(Grant *et al.*, 2014). The detrital phases within the sedimentary rocks are likely derived from the igneous rocks of the northern Gale Crater rim (Treiman *et al.*, 2016), which are 3.6–3.8 Ga (Thomson *et al.*, 2011; Le Deit *et al.*, 2013). The K-Ar ages of the detrital minerals in Cumberland and Mojave 2 are consistent within their uncertainties with the crater counts, but in both cases, are older than the crater counts. However, there is also significant uncertainty in the absolute calibration of martian crater density, which is primarily based on the lunar record, as discussed in the introduction (*e.g.*, Hartmann and Neukum, 2001; Neukum *et al.*, 2001). Given the paired uncertainties in crater counts and *in situ* K-Ar dating, the current set of Curiosity dates is broadly consistent with crater counts but is insufficient for refining the formation age of the geological unit surrounding Gale Crater better than our current estimates.

3.2. Cosmic-ray exposure ages

Based on ^3He , ^{21}Ne , and ^{36}Ar measurements, the calculated cosmic-ray exposure ages for Cumberland yielded a relatively geologically short surface exposure time of 72–84 Ma (Farley *et al.*, 2014). The exposure age of the Cumberland sample, if caused by uniform denudation, would correspond to 2–3 m in 78 Myr, or a few cm per Myr, though Newsom *et al.* (2015) estimated that this rate could be as slow as a few mm per Myr. However, Farley *et al.* (2014) argued that the relative elemental production rates are not consistent with steady erosion, and that the denudation of the Cumberland mudstone was caused by a common martian geomorphic process, scarp retreat. Measurements of similar scarps in the Yellowknife Bay region show an accumulated retreat of 60–80 m, or a lateral erosion rate of ~ 1 m/Myr.

The Windjana data yield a weighted mean exposure age of ~ 45 Myr $\pm 140\%$ (Vasconcelos *et al.*, 2016), corresponding to a denudation rate of approximately 4–5 m/Myr. This is about twice as fast as Cumberland, though the uncertainty encompasses the Cumberland age, implying that a scarp-retreat erosion mechanism is likely also occurring in the area where Windjana was drilled. The cosmic-ray exposure data provide guidance on future sampling strategies, where material protected from cosmic-ray irradiation may be accessible by relatively shallow drilling or digging under a scarp.

The results from the Mojave 2 sample were not as straightforward. Mojave 2 contains an extremely high abundance of ^3He , suggesting an exposure age of ~ 1 Ga, but the calculated exposure age from ^{36}Ar appears to be less than 300 Ma (however, buildup of H^{35}Cl contributed to a large uncertainty in ^{36}Ar). The apparent discrepancy between the ^{36}Ar and ^3He measurements, if interpreted in the framework of regional scarp retreat, would imply that the detrital grains in the Mojave 2 sample remained at the surface for ~ 1 Ga before burial and diagenesis. Alternatively, or additionally, the assumption of a uniform exposure model may be misleading. The production rates of noble gases by spallation and neutron capture reactions depend not only on the incoming energy but also on rock depth, atmospheric thickness, and abundance of Cl and H in the target material. Variability in these quantities over time and/or input from exogenous noble-gas-rich sources (such as interplanetary dust particles) may lead to nonuniformity in the sediment package being investigated.

3.3. Chronology of the Gale Crater sedimentary system

The Curiosity radiometric and cosmic-ray exposure ages from the three experiments (Table 1) help describe more fully the geological setting and history of the Curiosity landing site. The sedimentary mudstones and sandstones of the Murray and Stimson formations in Gale Crater contain a detrital, basaltic mineralogy recognized by the full complement of igneous minerals in the CheMin results, including relatively mechanically weak minerals such as plagioclase and pyroxene in Cumberland and Mojave 2. These detrital minerals likely represent the basalts of the highlands that surround Gale, some of which experienced exposure to cosmic-rays before being eroded during the active sedimentary system. The plagioclase appears to retain its igneous crystallization age, dating the basaltic highlands to approximately 4.0–4.2 Ga, which is roughly consistent with the crater density ages of these areas.

The sedimentary system within Gale Crater is estimated to have been active 3–3.5 Ga in a relatively warm and clement environment (Grotzinger *et al.*, 2015; Mahaffy *et al.*, 2015). After deposition, the sedimentary package underwent diagenesis, perhaps in multiple episodes (Rampe *et al.*, 2017). The Mojave 2 geochronology results show that one such episode of fluid flow permeated the Murray Formation around 2 Ga, depositing salts associated with more acidic conditions. This age is corroborated by the presence of Amazonian-aged alluvial fans and chloride deposits near Gale (Grant *et al.*, 2014; Ehlmann and Buz, 2015). These episodes of aqueous activity created features such as veins and concretions, as well as cementing material, and may also have been responsible for weakening the rocks and causing mechanical breakup.

The northern slope of Mt. Sharp then experienced extensive denudation, as evidenced by the nearly continuous lower surface of the Murray formation and the discontinuous capping Stimson Formation. The short surface exposure ages measured by Curiosity suggest that the current landscape is currently being denuded by removal of these materials by episodic scarp retreat facilitated by aeolian scouring to remove material.

4. Improving the Absolute Chronology of Mars

Several measurements contribute to the Curiosity K-Ar ages, including the APXS measurement of the bulk potas-

sium in the sample, the SAM measurement of ^{40}Ar , the sample mass passed to SAM by CHIMRA, and, for Mojave 2, the partitioning estimates of the potassium among minerals. The bulk potassium content has an accuracy of 15% of the measured value (Martin *et al.*, 2017). The ^{40}Ar abundance has an uncertainty associated with subtracting background measurements and hydrocarbon interferences, but because these are measured contemporaneously with the noble gases, the associated uncertainty is quite small (generally less than 1–2%; *e.g.*, Martin *et al.*, 2017). The sample mass is derived from engineering tests and models, with a relative uncertainty of $\sim 13\%$ (Farley *et al.*, 2014). The uncertainty associated with modeling the K partitioning among mineral fractions depends both on the model assumptions of K abundance in specific mineral phases and on the uncertainty in the CheMin measured weight fractions; as such, the uncertainties are best discussed as a function of model assumptions, as in the work of Martin *et al.* (2017). Curiosity's measurement of the detrital minerals in Cumberland had an uncertainty of 8.3%, and the model ages of the Mojave minerals had uncertainties of 15–17% (1σ).

The principal drawbacks of the Curiosity geochronology experiments that result in diminished confidence in their precision and accuracy include the following: (1) Measurement of parent K and daughter Ar is performed on two different aliquots of the sample, without a reliable method to ensure they are the same after processing and delivery through CHIMRA. Measurement of parent and daughter isotopes on the same aliquot of sample would ensure that minerals and grain sizes are not being sorted as the samples are portioned. (2) The relatively low maximum oven temperature in SAM is not high enough (and rover operational constraints prevent it from operating long enough) to completely outgas highly retentive minerals, such as sanidine, as seen in the Windjana experiment. Complete collection of both parent and daughter isotopes from an aliquot is required for an accurate measurement. (3) The development and implementation of the measurement techniques rely on known functionality of the instruments along with multiple assumptions. For example, geochronology runs use a SAM semi-static mode that relies on partially closing a high-conductance valve to increase the signal for low-abundance species (Mahaffy *et al.*, 2012; Atreya *et al.*, 2013). This partially dynamic environment introduces uncertainty in the abundance of the species versus gain of the detector. In

TABLE 1. SUMMARY OF CURIOSITY RADIOMETRIC AND COSMIC-RAY EXPOSURE AGE EXPERIMENTS

Location	Aliquot	Radiometric age (Ma)	CRE age (Ma)	Interpretation
Cumberland		4210 ± 350 (8.3%)	78 ± 6 (7.7%)	Crystallization age of detrital minerals from basaltic precursor; mm to cm/Ma denudation by scarp retreat
Windjana	Aliquot 1	627 ± 50 (8.0%)	145 ± 203 (140%)	Radiometric ages inaccurate due to incomplete degassing and/or mineralogic fractionation during sample handling
	Aliquot 2	1710 ± 110 (6.4%)		
Mojave 2	Plagioclase	4070 ± 630 (16%)	300 (^{36}Ar) to 1000 (^3He)	Crystallization age of detrital minerals from basaltic precursor; pre-burial exposure
	Jarosite	2120 ± 360 (17%)		Fluid flow through the Murray bedrock

Ma, millions of years before present.

terrestrial samples, ^{40}Ar may be measured by ratio to the abundant stable isotope ^{36}Ar (Solé, 2014), but the $^{40}\text{Ar}/^{36}\text{Ar}$ ratio on Mars is far higher and the abundance of chlorine in the surface materials leads to high concentrations of isobaric HCl. The amount of sample is another large source of uncertainty, because the sample mass or volume (or more correctly, the moles of sample) is used to derive absolute Ar abundance. On Curiosity, there is no independent way to verify the sample amount delivered to SAM, introducing uncertainty. Not all uncertainties in any method can be known or calibrated in advance, but the use of an onboard age standard would go a long way toward ensuring accuracy and demonstrating precision. (4) Uncertainty in the geological interpretation of the measured sample and its history of gain and loss of parent and daughter lead to unknown accuracy. This is not unique to the Curiosity experiments and needs to be addressed for all potential systems via supporting measurements, such as mineralogy and geomorphology.

The capability of flight instruments to conduct *in situ* geochronology is specified in the NASA Planetary Science Decadal Survey and the NASA Technology Roadmap (National Research Council, 2011; National Aeronautics and Space Administration, 2015) as needing development to serve the community's needs. To make significant advances in creating a geochronological framework, *in situ* geochronology must yield ages that are both precise and accurate—that is, the measurement techniques must yield small uncertainties on the calculated age, and that age must be recognizable and interpretable as a geological event. The NASA Technology Roadmaps suggest a minimum precision better than ± 200 Ma (or $\pm 5\%$ over 4.5 Ga), or about $2\times$ better than the precision currently achieved by Curiosity, and a desired precision of ± 50 Ma (or $\pm 1\%$ over 4.5 Ga).

Doran *et al.* (2004) outlined multiple chronometric techniques that might be used to provide absolute dates on events in martian planetary history, including radiometric isotope dating (*e.g.*, K-Ar, Rb-Sr, and U-Th-Pb systems), cosmogenic nuclide dating, dosimetry-based methods (*i.e.*, luminescence), and exploitation of processes on Mars such as variation in atmospheric stable isotopes and flux of extraterrestrial material. For many planetary materials, it may be possible to measure ages by using more than one system, which is common practice in terrestrial laboratory geochronology. Agreement between multiple chronometers increases confidence in the interpretation of the geological events experienced by the sample, though disagreement does not negate the inherent value of each measurement.

Multiple groups have made substantial progress on bringing some of these techniques closer to flight implementation. Here, we discuss these techniques and compare them with the current Curiosity measurements. At present, none are stand-off or remote techniques; all share a common need for sample acquisition and handling with a greater or lesser degree of complexity.

4.1. K-Ar

K-Ar is a robust choice for *in situ* implementation given the relatively high abundance of K in martian rocks and the ability to release and measure K and Ar by different methods, thus avoiding isobaric interferences. The AGE (Argon Geochronology Experiment) collected a powdered sample

in a cup and released argon by heating the sample, similar to the Curiosity experiment, but measured the sample's potassium concentration by laser-induced breakdown spectroscopy (LIBS) and determined the volume of rock from which Ar was released by estimating the volume of the melted sample (Swindle *et al.*, 2003; Fennema *et al.*, 2007). This would have produced a bulk K-Ar age on the sample by measuring K and Ar on the same aliquot, but the oven required a large power draw to achieve high temperatures and full degassing that was inconsistent with typical flight instruments.

Farley *et al.* (2013) developed a method that would also measure a powdered sample by heating in a cup, again similar to Curiosity, but introduced two improvements. First, the cups would be preloaded with a flux to enable complete melting and degassing of both Ar and K at the oven temperatures achievable on planetary missions. Second, the cups would also be preloaded with a small isotopic spike to enable mass spectrometry (MS) by the double spike - isotope dilution technique. This would provide an onboard standard measured with each experiment to ensure accuracy and monitor instrumental effects. The advantage to both these approaches is their ability to measure K and Ar on the same sample rather than by split aliquots, and in the latter case, to achieve complete degassing and compare with an onboard standard. The precision achievable by the double spike - isotope dilution method was estimated to be $\pm 5\%$ (1σ) (Farley *et al.*, 2013). Both would be resource-intensive to the mission, requiring sample drilling and portioning, along with finite cups (and flux/spike if included), limiting the number of samples that could be analyzed. Both would also be bulk measurements and because of the resource constraints, repeat experiments for verification would need to be weighed against sample diversity.

Several laboratories have developed breadboards that would provide multiple measurements on a single solid sample by measuring K and Ar using a combination of LIBS to measure parent K, and MS to measure daughter Ar (Cohen *et al.*, 2014; Solé, 2014; Cho *et al.*, 2016; Devismes *et al.*, 2016; Cho and Cohen, 2018; Cattani *et al.*, 2019). These LIBS-MS instruments completely release Ar from small pits by laser ablation (LA) rather than oven heating and admit the released gas to the MS. Using LA enables the technique to be applied to solid, unprepared samples such as chips or pebbles rather than powders, and surface contamination can be ablated away before analysis.

LIBS-MS also permits multiple laser measurements to be made on a single sample, creating a linear array of measurements with a slope proportional to the age of the rock (an internal isochron). Use of isochrons decreases measurement uncertainty and increases the robustness of the interpretation. The isochron approach also obviates the need to independently assume or determine any initial or trapped contributions to ^{40}Ar in a bulk sample.

The LIBS-MS family of instruments is especially promising for near-term implementation because its components (LIBS, MS, and cameras to measure the ablation pit volume) have successfully flown aboard the Curiosity and Rosetta missions. The quantification of elements by LIBS and the volume measurement by optical metrology are relatively imprecise compared with MS and lead to an estimated uncertainty of $\pm 8\%$ to 16% (1σ) in individual measurements, with better precision potentially achievable by using

multiple-point isochrons (Cohen *et al.*, 2014, Cho and Cohen, 2018), approaching the guidelines set out in the NASA Technology roadmap.

Morgan *et al.* (2017) investigated the requirements for an ^{40}Ar - ^{39}Ar system to be used for *in situ* applications. The ^{40}Ar - ^{39}Ar method is based on the K-Ar method, where fast neutrons are used to convert some stable ^{39}K to ^{39}Ar , and measurement of ^{39}Ar serves as a proxy for the parent isotope ^{40}K . After irradiation, incremental heating of samples can be used to interrogate the thermal history and age of the sample. For *in situ* applications, developing an instrument with sufficient neutron fluence to create measurable amounts of ^{39}Ar values in reasonable timeframes would be challenging. High-sensitivity mass spectrometers would also be required to measure a low ^{39}Ar signal given isobaric interferences from hydrocarbons and chlorine compounds in the mass range of interest (m/z [mass-to-charge ratio]=36–40), which have also bedeviled the Curiosity experiments (Farley *et al.*, 2014). However, if implementable, an advantage of using the Ar-Ar system would be that step-heating could help reveal a complex sample's thermochronometric history, engendering higher confidence in its accuracy and interpretation.

In addition to radioisotope geochronology, the Curiosity measurements have shown the power of measuring noble gases to retrieve cosmic-ray exposure ages, therefore becoming an important goal for all instruments that are capable of mass spectroscopy. The drawbacks to the Curiosity method relate to the abundance of the nuclides, the sensitivity of the mass spectrometer, and isobaric interferences. To concentrate the noble gases for analysis, SAM uses a semi-static mode of operation to achieve concentrations ~ 10 times higher than the normal, low-sensitivity mode of operation. However, SAM also has experienced an internal buildup of hydrocarbons and HCl, making low-abundance measurements of the cosmogenic noble gases such as ^{36}Ar more difficult to measure. The SAM experience highlights the need for reproducible standards to be added to *in situ* techniques that ensure accuracy, provide confidence in the results, and enable long-term monitoring to ameliorate instrument degradation.

4.2. Rb-Sr

^{87}Rb - ^{87}Sr geochronology is extensively used for Solar System materials because of its long half-life (49.2 Gyr) and differential behavior of parent and daughter in geological settings: Rb is highly incompatible, whereas Sr concentrates in crystallizing minerals, primarily plagioclase. The principal challenge with this system is that parent and daughter are isobaric, requiring mass resolution better than $m/z=300,000$ to distinguish them. Rather than create a mass spectrometer with such high mass resolution, two groups have attempted development of this system for *in situ* applications using different approaches. Similar to the K-Ar and Ar-Ar methods described earlier, Rb-Sr instruments require sample acquisition and analysis in a sealed and evacuated chamber to prevent ions liberated from the sample from escaping and to enable quantitative correlation of parent and daughter.

Coleman *et al.* (2012) reported laboratory testing of an inductively coupled plasma ionization source coupled to multi-collector mass spectrometry, following the work of Ramos *et al.* (2004). This method measured total ionic yield

at mass 86 as a proxy for Sr and at mass 85 for Rb, used a mathematical conversion of Rb concentration ratios to arrive at ^{87}Rb , and calculated ^{87}Sr by its ratio to ^{84}Sr (which was, in turn, corrected for the contribution of ^{84}Kr by reference to ^{80}Kr). This technique is a variant of traditional K-Ar and U-Pb “chemical dating,” where elemental abundances are measured, and it is assumed that the radioactive decay product is the only isotope present for its element. Application in this way assumes that variations in ^{87}Sr resulting from radioactive decay produce only minor variations in overall Sr abundance; therefore, this assumption is only valid for minerals that have a very high Rb/Sr ratio, such as biotite, otherwise the high concentration of common Sr in most materials makes it impossible to determine $^{87}\text{Sr}/^{86}\text{Sr}$ with useful precision (Vroon *et al.*, 2008).

Anderson *et al.* (2015a, 2015b) have developed a resonance ionization-mass spectrometry (RIMS) method for *in situ* Rb-Sr dating. Sampling would be done by LA, which produces a few ions, but the plume of mainly neutral species is then subjected to a secondary series of lasers tuned to each species that progressively excites and finally ionizes each one separately. This method elegantly separates the isobaric parent and daughter and allows them to be independently introduced into a mass spectrometer via ion optics. Similar to the LIBS-MS for K-Ar, the LA-RIMS method would produce an internal isochron from multiple spots on the same sample, increasing confidence in the interpretation.

The performance of the LA-RIMS instrument has been demonstrated on the martian meteorite Zagami (160 Ma) and the terrestrial Duluth gabbro (1096 Ma) (Anderson *et al.* 2015a, 2015b). For both samples, measurement precision of ± 100 –200 Ma was achieved. For Zagami, as for most young samples, this accuracy and precision (± 30 –50%) are outside the desiresments of the NASA Technology Roadmap, but the performance on older rocks is approaching the guidelines in the NASA Technology Roadmap. Further development of instrument requires preparation of a flat surface on the sample for analysis (by cutting or grinding) and miniaturization and ruggedization of the different sets of tuned lasers.

4.3. Pb-Pb

Riedo *et al.* (2013) demonstrated Pb-Pb dating by using an LA ion source and a miniaturized reflectron-time-of-flight mass spectrometer, developed for use on planetary missions. At optimal conditions, measurements of Pb isotope compositions in lead-rich standards and natural terrestrial samples were performed with uncertainties at per mil levels, translating to $^{207}\text{Pb}/^{206}\text{Pb}$ ages with precision in the range of tens of millions; the relative accuracy and precision of the measurements would be significantly degraded for samples with Pb isotopic concentrations lower than 100 ppm, as is typical for many planetary rocks. Anderson (2017) also showed preliminary results by using LA-RIMS with different wavelength lasers that may also be used to excite and ionize Pb for dating in this system. Although Pb-Pb system measurements are technically promising, their potential for geochronology may be limited by our knowledge, where mixing among poorly known Pb reservoirs on the Moon and Mars may inhibit accurate interpretations of the data.

4.4. Luminescence

Dosimetric techniques that have the potential to date martian sedimentary events include thermoluminescence, optically stimulated luminescence, and electron spin resonance. These methods would quantify the rate of accumulation of free electrons from exposure to natural ionizing radiation within mineral grains. Over time, ionizing radiation from the decay of naturally occurring radionuclides and from cosmic-rays liberates charge carriers within mineral grains, leading to the accumulation of a “trapped” charge. When exposed to solar radiation, the trapped charge population is depleted, thereby resetting the clock. In practice, a sample is exposed to thermal or optical stimulation, and the intensity of the emitted luminescence is proportional to the dose absorbed since the last exposure to sunlight, dating the time since burial (*i.e.*, the depositional age). The limiting age for luminescence effects is determined by saturation of the luminescence signal, because there is a finite concentration of defects in the material at which charge can be localized (Doran *et al.*, 2004; Sears, 2013).

Luminescence may have potential for dating of martian sedimentary processes, such as the frequency of aeolian dust storms, polar layering, and fluvial activity (McKeever *et al.*, 2003, 2006; Jain *et al.*, 2006; Sohbati *et al.*, 2012). Luminescence dating typically concentrates on quartz and feldspar, because lattice defects or impurities in these minerals enable buildup of trapped charge. Conversely, iron-bearing materials dilute the optically stimulated luminescence effect, such that they may need to be separated and discarded before measurement if they have grain sizes smaller than the source of the stimulation. For a rover- or lander-based instrument, material would be collected from the surface via an arm with a scoop or drill, deposited into a sample hopper for grain size and magnetic separation, and transported from the sample hopper to the analysis and irradiation chambers (DeWitt and McKeever, 2013).

The possible range in ages determinable by luminescence dating on Mars, assuming reliable doses can be measured close to apparent saturation, is approximately 40–600 ka (Jain *et al.*, 2006; Sohbati *et al.*, 2012). Complex mineralogy, poorly defined sample grain size distributions, high cosmic-ray dose rates, anomalous fading, and low temperatures are among the challenges that need to be addressed in determining the success of martian luminescence dating.

5. The Future of Martian Geochronology

The absolute ages of Mars’s geological events, and thus the time history of the planet’s evolution, will not be fully understood until the relative martian chronology derived from stratigraphy is tied to an absolute chronology via radiometric dating of martian rocks. Formation and exposure ages of astrobiologically relevant rocks being investigated by Curiosity, coupled with their overall mineralogy and volatile content, will reveal when during the history of the planet the prevailing conditions that formed and weathered the rock occurred.

A wide variety of martian surface rocks lend themselves to investigation with *in situ* geochronology. Igneous rocks are the most well known, giving constraints on crystallization age of magmatic bodies. Igneous textures and compositions were observed by Curiosity in numerous float rocks, where

ChemCam analyses generally reflect a felsic composition (Sautter *et al.*, 2014; Schmidt *et al.*, 2014). The first rock examined in detail by Curiosity, Jake Matijevic (Jake_M), has an igneous texture on the surface observed at MAHLI scale, and an alkali-rich composition deduced from APXS and ChemCam chemistry (Stolper *et al.*, 2013). Other rocks exhibit a coarse-grained texture typical of slowly cooled magmatic rocks, including dark millimeter-wide phenocrysts typical of mafic phases (*i.e.*, pyroxene or olivine), separated by light-toned matrix likely dominated by feldspars (Sautter *et al.*, 2014).

In addition to a strictly igneous origin, there is also the possibility that some of the rocks could represent rocks derived from impact melts (Newsom *et al.*, 2015). Though igneous rocks hold promise and potential as targets for geochronology, dating experiments are limited by what Mars provides and the abilities of the mission to sample them. On Curiosity, the mechanical action of the drill requires sampling bedrock targets, which are all sedimentary at Gale Crater. The Curiosity drill must be placed against a flat surface and has no backstop mechanism, so irregular float rocks such as Jake_M may be pushed away. Alternative acquisition strategies may help to acquire ages on pieces of igneous rocks that occur as float in the sedimentary systems favored by rover exploration, but a mission to a large, well-characterized igneous province on Mars, carrying one or more geochronology instruments, would be a powerful way to constrain the martian impact flux and anchor the absolute age calibration for Mars (Tanaka *et al.*, 2014; Anderson *et al.*, 2015b; Morgan *et al.*, 2017).

Curiosity is currently climbing Mt. Sharp, composed of now-eroded sedimentary layers within central Gale Crater. Pre-landing interpretations of Mt. Sharp include lower sediment layers that may have originally been deposited on a lake bed, whereas observations of possibly cross-bedded strata in the upper mound suggest aeolian processes (Anderson, 2010). Additional possible sources for layered materials include volcanoclastic and distal ejecta deposits (Newsom *et al.*, 2015). This package of sedimentary rocks may also have phases that are dateable by using the K-Ar system. Potassium is higher than expected for the mineralogy in some Curiosity-investigated rocks, possibly residing in alteration minerals or secondary phases such as phyllosilicates and jarosite (Fisk *et al.*, 2014; Le Deit *et al.*, 2016). Absolute ages of lithologies containing these minerals are important in understanding the transitional period in martian history between the epoch of flowing surface water and the current arid climate, one marked by widespread ground-water mobilization and diagenesis.

Curiosity may not be able to provide more absolute ages. Failure of the drill bit retraction mechanism that feeds sample to the CHIMRA occurred in December of 2016. Curiosity has resumed drilling by leaving the drill bit extended and using percussive as well as rotary force. The sample collected in the drill bit is now dropped directly into the instrument sample inlets, bypassing the sieving and sample portioning capability of CHIMRA. The lack of accurate portioning precludes further dating experiments, because sample mass is a crucial input to interpretation of the age. The Curiosity team is working on alternative methods to estimate sample portioning to be able to continue these important experiments.

The Curiosity measurements have served to validate radiometric dating techniques on Mars and guide the way for future instrumentation to make more precise measurements, ensure that fundamental dating assumptions are valid, and enable interpretation of the geological events recorded by the radiometric age. Though the rover is aging and future *in situ* dating with Curiosity is uncertain, it is important to continue the quest for absolute dating of martian rocks. Continued investment in *in situ* dating techniques is needed so that geochronology instruments can be selected and flown in the 2020s and 2030s. These investments are crucial to be able to provide meaningful constraints on geological and astrobiological events on Mars and interpret martian history within the context of the wider Solar System.

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Address correspondence to:

Barbara Cohen

NASA Goddard Space Flight Center

Mail Code 698

Greenbelt, MD 20771

E-mail: barbara.a.cohen@nasa.gov

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Abbreviations Used

APXS = Alpha Particle X-Ray Spectrometer
 CHIMRA = Collection and Handling for *In-Situ*
 Martian Rock Analysis
 LA = laser ablation
 LIBS = laser-induced breakdown
 spectroscopy
 m/z = mass-to-charge ratio
 MAHLI = Mars Hand Lens Imager
 MS = mass spectrometry
 MSL = Mars Science Laboratory
 Myr = millions of years
 RIMS = resonance ionization–mass
 spectrometry
 SAM = Sample Analysis at Mars